

Symmetry-enhanced supertransfer of delocalized quantum states

Seth Lloyd^{1,2} and Masoud Mohseni^{2,3}

¹*Department of Mechanical Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge MA 02139*

²*Center for Extreme Quantum Information Theory, Research Laboratory of Electronics, Massachusetts Institute of Technology, Cambridge, MA 02139*

³*Center for excitonics, Research Laboratory of Electronics, Massachusetts Institute of Technology, Cambridge, MA 02139*

Coherent hopping of excitation rely on quantum coherence over physically extended states. In this work, we consider simple models to examine the effect of symmetries of delocalized multi-excitation states on the dynamical timescales, including hopping rates, radiative decay, and environmental interactions. While the decoherence (pure dephasing) rate of an extended state over N sites is comparable to that of a non-extended state, superradiance leads to a factor of N enhancement in decay and absorption rates. In addition to superradiance, we illustrate how the multi-excitonic states exhibit ‘supertransfer’ in the far-field regime: hopping from a symmetrized state over N sites to a symmetrized state over M sites at a rate proportional to MN . We argue that such symmetries could play an operational role in physical systems based on the competition between symmetry-enhanced interactions and localized inhomogeneities and environmental interactions that destroy symmetry. As an example, we propose that supertransfer and coherent hopping play a role in recent observations of anomalously long diffusion lengths in nano-engineered assembly of light-harvesting complexes.

PACS numbers:

Recent works on quantum coherence of photosynthesis has revealed a rich tapestry of coherent and incoherent interactions in excitonic hopping processes [1–10]. Natural selection may well have tuned the tradeoffs between coherent hopping, decoherence, dissipation, and the non-Markovian nature of the phonon environment, to arrive at robust and highly efficient energy transfer methods [3, 9]. As is typical of biological systems, the highly-evolved final product of evolution exhibits a complexity which reflects the different types of apparatus required to take advantage of the rich range of dynamical effects at the microscale. While efficient from an evolutionary standpoint, this complexity can mask the essential simplicity of the underlying the quantum effects that allow energy transfer to take place in the first place.

One of the key features of excitonic energy transfer in photosynthesis is the extended, delocalized nature of the states involved in the hopping process. This extended form of the states is enforced from the very moment of photon absorption: because the wavelength of light is large compared with the atomic scale, a very large numbers of electrons participate coherently in the initial absorption process, and the resulting initial excitonic state extends over a large number of atoms or molecules. This paper looks at the dynamics and environmental interactions of states that extend over N atoms, and uses simple quantum models to establish some general features of such interactions.

First of all, states that interact symmetrically with a collection of bosons (phonons or photons or both), exhibit the normal N -fold superradiant enhancement of emission and absorption in both the resonant and non-resonant regimes [11–16]. Superradiance, of course, follows directly from the symmetrized nature of the atom-boson interaction. Interactions that break that symmetry can lead to non-radiant excited states, multiple-site analogues of the non-radiant two-site antisymmetrized singlet state. By contrast, environmental

interactions such as decoherence that do not rely on energy exchange exhibit no ‘super’ enhancement of the decoherence rate of single-exciton states due to symmetry.

We employ a second-quantized spin-boson notation that allows the treatment of multiple excitonic states. For multiple excitonic states, the decoherence rate can either be enhanced or decreased, depending on the nature of the correlations between the multiple excitons. Symmetrized states of n excitons spread amongst N sites exhibit the usual superradiant factor of $(N - n + 1)n$ in their emission rate. Antisymmetrized states of n excitons can have their emission rate largely suppressed, thereby providing a potential mechanism for exciton preservation in multi-site systems.

Decoherence or pure dephasing has a different dependency on exciton number: symmetrized states of n excitons coupled symmetrically to a common environment exhibit a decoherence rate that goes as n times the single exciton rate. In contrast, the decoherence rate of an uncorrelated n -exciton state, or a symmetric state coupled to an asymmetric environment, typically goes as \sqrt{n} times the single exciton rate. As in the case of emission, states in special antisymmetrized decoherence-free subspaces can have their decoherence rates largely suppressed.

The features of delocalized states interacting symmetrically with their environment described so far are well-known. In particular, the effects of inhomogeneous broadening (static disorder) and phonon-bath coupling on superradiance relaxation for molecular aggregates have been studied in detail [13–15]. Less familiar is the phenomenon of cooperative excitation energy transfer or supertransfer [17, 18]: consider an extended excitonic state over N sites that is hopping to an extended state over M sites. If the hopping interaction possesses the proper symmetries, then we show below that the overall hopping rate is proportional to MN , and enhancement of N over the hopping rate of a localized state hopping to one

of M sites. The supertransfer enhancement follows from the same symmetry considerations as superradiance, but it is essentially a radiationless relaxation. Under certain conditions where a molecular aggregate can coherently donate an excitation and an acceptor molecular aggregate can coherently receive it, then the dipole approximation and first-order perturbation for electronic coupling imply that we might observe supertransfer of excitation energy. Supertransfer also appears when the time-averaged site-site couplings γ_{ij} between each of the N sites and each of the M sites are largely similar. Cooperative excitation energy transfer can also occur in disordered chromophoric systems and light-harvesting complexes [18].

Symmetric enhancements of dynamical timescales extend to environmental interactions. An interaction between excitons at N sites and a set of bosonic modes (phonons, photons) can be decomposed into fully symmetrized interactions between the symmetric states over those sites and symmetrized bosonic modes, and into other interactions with different symmetries. The fully symmetrized interactions participate in the N -fold superradiant enhancement of interaction rates. Accordingly, these interactions participate more strongly in, e.g., symmetrized hopping interactions. Meanwhile, the other interactions tend to destroy the symmetry of the extended states and reduce hopping.

A full treatment of the various symmetries of interactions between spins, atoms, excitons, and bosonic environment modes would require a general treatment in terms of representations of the symmetric group using Young diagrams and tableaux. As the purpose of this paper is simply to examine the way in which superradiant enhancements ‘spill over’ into hopping and environmental interactions, we content ourselves here with a treatment of fully symmetrized states and leave the more general treatment for elsewhere [19].

SUPERTRANSFER IN SPIN-BOSON MODEL

We start by reviewing the ordinary picture of superradiance in the resonant interaction between N two-level atoms and a mode of the electromagnetic field. The Hamiltonian for this system is:

$$H = \hbar(\omega a^\dagger a - \omega/2 \sum_{j=1}^N \sigma_z^j + \gamma \sum_j \sigma_x^j (a + a^\dagger)). \quad (1)$$

For simplicity we have assumed that the oscillatory field is polarized along the x -axis. The ground state of each atom is $|0\rangle = |\uparrow\rangle$, and the excited state is $|1\rangle = |\downarrow\rangle$. The fully symmetrized state with n excited atoms is

$$|n\rangle \equiv \frac{1}{\sqrt{N}} \sum_{\pi \in S_N} |\pi(00 \dots 011 \dots 1)\rangle. \quad (2)$$

Here π is a permutation in the symmetric group over N elements, S_N , and there are n 1's and $N - n$ 0's in the state.

The states $|n\rangle$ are those that are obtained from the state $|N\rangle = |11 \dots 1\rangle$ by radiant decay, or from the state $|0\rangle = |00 \dots 0\rangle$ by stimulated absorption.

As Dicke pointed out, superradiance arises from the symmetrized nature of the states and their interaction with the field [11]. If we look at the decay rate of a single atom coupled to the field in its vacuum state, we find that its amplitude to first order in perturbation theory goes as γ , and its probability goes as γ^2 . By contrast, the decay amplitude of the symmetrized state $|n\rangle$ goes as

$$\begin{aligned} \langle m = 1 | \langle n - 1 | \gamma \sum_j \sigma_x^j (a^\dagger + a) | n \rangle | m = 0 \rangle \\ = \sqrt{n(N - n + 1)} \gamma, \end{aligned} \quad (3)$$

where m labels the photon number in the mode. The decay probability goes as $n(N - n + 1)\gamma^2$. Comparing the decay rate of the one-excitation symmetrized state $|n = 1\rangle$ with that of the single-atom decay rate, we see that the symmetrized state decays N times as fast. By contrast, the stimulated emission rate for the symmetrized state is the same as the incoherent stimulated emission rate.

Symmetry can enhance more than the spontaneous emission rate. Let's turn to hopping and look what happens when an excitonic state that is symmetrized over N sites hops to an excitonic state that is symmetrized over M sites via a symmetric coupling [17]. In this idealized case, the symmetrized hopping Hamiltonian is

$$H = \hbar \left(-\frac{\omega_A}{2} \sum_{j=1}^N \sigma_z^j - \frac{\omega_B}{2} \sum_{k=1}^M \sigma_z^k + \gamma \sum_{j=1, k=1}^{N, M} \sigma_+^j \sigma_-^k + \sigma_-^j \sigma_+^k \right). \quad (4)$$

Here, j labels the A sites and k labels the B sites. Performing the same calculation as in superradiance, but taking into account the symmetrized nature of both the A and B states, shows that the rate of hopping of an excitation from the symmetrized state $|n\rangle|m\rangle$ to the symmetrized state $|n-1\rangle|m+1\rangle$ goes as $\gamma^2 n(N - n + 1)(m + 1)(M - m)$. Taking into account transfer from B to A as well as from A to B , we find that the overall transfer rate from A to B , starting in the state $|n\rangle|m\rangle$, goes as

$$\gamma^2 (n(N - n + 1)(m + 1)(M - m) - (n + 1)(N - n)m(M - m + 1)), \quad (5)$$

where the first term represents the rate of an excitation hopping from A to B and the second term represents the rate of hopping from B to A . For a single symmetrized excitation hopping from the A states to the B states we see that the rate of transition from $|n = 1\rangle|m = 0\rangle$ to $|n = 0\rangle|m = 1\rangle$ goes as $\gamma^2 NM$: that is, the hopping rate between symmetrized single excitation states goes as NM times the hopping rate of an excitation between one of the A sites to one of the B sites. For higher numbers of excitations, we see that the quartic terms in equation (5) cancel out, leaving only cubic terms. For example, when there are $O(N)$ excitations in A ,

and $O(M) < O(N)$ excitations in B , the transfer rate from A to B goes as $O(N^2M)$.

Similar supertransfer due to partial symmetry may be relevant to various hopping processes in photosynthetic light-harvesting (LH) complexes [13–15], within the context of generalized Förster theory [18, 20–22]. In the typical treatment of Frenkel exciton in these systems, the transfer rate is calculated from the transition probability of an excitation hopping from one molecule to another using Förster Resonance Energy Transfer (FRET) based on dipole-dipole interaction of individual molecules and perturbation theory (Fermi’s golden rule). However, due to strong interactions of a group of molecules the excitation can become highly delocalized. Thus, one can introduce a huge (effective) dipole moment associated with each group leading to an enhanced oscillator strength. Consequently, the rate of exciton dynamics can be calculated from these effective very large dipole-dipole interactions even in the far-field within the dipole approximation. A closely packed group of N molecules under certain symmetry can collectively accept or donate an excitation with a rate which is almost N times faster than each individual molecule.

Consider, for example, the rate of hopping of a single exciton from a ring containing N chromophores to a ring containing M chromophores. If the chromophores are spread evenly along each ring, then the lowest energy states single-exciton states in each ring are in fact the fully symmetric $|n = 1\rangle$ and $|m = 1\rangle$ states. If the two rings are distant from each other and coupled, e.g., via dipolar Förster forces, then the couplings of the chromophores between rings are approximately symmetric. Accordingly, the rate of hopping from the A ring to the B ring is NM times the rate of the rate of an exciton hopping from a chromophore on the A ring to a chromophore on the B ring. The hopping enhancement arises because hopping between symmetrized states is essentially a kind of superradiance where the A states ‘emit’ their excitonic energy into the B states. Circular symmetry of the above nature exists in LHI and LHII of purple bacteria [23].

SYMMETRY PROPERTIES OF DELOCALIZED STATES UNDER ENVIRONMENTAL INTERACTIONS

There are many other effects in real quantum systems including diagonal and off-diagonal static disorders, couplings of excitonic states within a single ring, and phonon-bath couplings. If $\omega_A \neq \omega_B$, then the excitonic transfer must be accompanied by energy transfer to/from the environment. Now, just as the effects of symmetry translated directly over from superradiance to supertransfer, we will show that symmetry can similarly enhance the effects of environmental interactions. Let’s include intra-ring couplings and add bosonic environments to the A and B states, so that our overall Hamiltonian is

nian is

$$\begin{aligned}
 H = \hbar \bigg(& -\frac{\omega_A}{2} \sum_{j=1}^N \sigma_z^j + \sum_{\ell} \omega_{A\ell} a_{\ell}^{\dagger} a_{\ell} + \sum_{j\ell} \Gamma_{j\ell} H_{j\ell} \\
 & -\frac{\omega_B}{2} \sum_{k=1}^M \sigma_z^k + \sum_{\ell'} \omega_{B\ell'} a_{\ell'}^{\dagger} a_{\ell'} + \sum_{k\ell'} \Gamma_{j\ell'} H_{j\ell'} \\
 & + \gamma \sum_{j=1, k=1}^{N, M} \sigma_+^j \sigma_-^k + \sigma_-^j \sigma_+^k \\
 & + \sum_{j, j'=1}^N \gamma_{jj'} (\sigma_+^j \sigma_-^{j'} + \sigma_-^j \sigma_+^{j'}) \\
 & + \sum_{k, k'=1}^M \gamma_{kk'} (\sigma_+^k \sigma_-^{k'} + \sigma_-^k \sigma_+^{k'}) \bigg). \tag{6}
 \end{aligned}$$

Here $H_{j\ell}$ is some suitable interaction between the j ’th spin and the ℓ ’th mode, e.g., $\gamma_{j\ell} (a_{\ell}^{\dagger} \sigma_-^j + a_{\ell} \sigma_+^j)$.

The γ term represents the symmetric inter-ring coupling, and the $\gamma_{jj'}$, $\gamma_{kk'}$ terms represent the intra-ring couplings within the A and B rings respectively. Note that even with intra-ring hopping couplings, because of the symmetric arrangement of chromophores in the ring, the fully symmetric single exciton state within each ring is the ground state of the single-exciton sector.

The key feature of this Hamiltonian (and of similar multiple-spin/multiple boson models) is that the environmental interaction can contain a significant component that is coupled directly to the symmetrized states $|n\rangle$. This is true even if the general interaction takes the form of interactions between local sites and local modes as above. The insight here is that, because the interaction is linear in the a_{ℓ} , a_{ℓ}^{\dagger} and the Pauli matrices, we are always free to perform a Bogoliubov transformation on the modes to identify modes corresponding to delocalized, symmetrized bosonic excitations. In the case of chromophoric ring, as above, these excitations are simply the global symmetrized vibrational modes of the ring itself. That is, if each site is coupled to a localized phonon mode with frequency ω , then we are free to define a delocalized, symmetric phonon mode with frequency ω : the symmetrized states of the ring are then coupled to this symmetrized phonon state with the usual superradiant factor of N .

Now, just as in superradiance, the amplitude in first order perturbation theory for the destruction of a symmetrized excitation of the spins and the creation of a symmetrized excitation of the bosonic modes is proportional to $\sqrt{n(N-n+1)}$. Moreover, in the overall Hamiltonian (6), we can extract out the symmetrized sectors of spin states and bosonic states in A and B respectively. Transitions between these states, including those that involve emission of energy into the symmetrized phonon modes, all involve superradiant enhancements. As the case of hopping shows, when an N -site symmetrized state exchanges energy via a symmetric interaction with an M -site

state, the enhancement of the interaction rate goes as the product $n(N - n + 1)(m + 1)(M - m)$, where n, m are the excitation number of the symmetrized states, including now the states of the symmetrized bosonic modes, and the net transfer of energy goes as equation (5). While the case of excitonic hopping is frequently restricted physically to the interactions of a few excitons at a time, the symmetrized modes of the bosonic bath can readily contain a large number of phonons, so that the extra factors of n, m can really ‘kick in’ and enhance the transfer of energy from excitonic states to the bath, and back to excitonic states again. As equation (5) shows, the rate of transfer grows as a cubic function of the populations and site numbers.

We can now formally decompose the Hamiltonian of equation (6) into cooperative and ‘normal’ sectors. The cooperative sector consists of the symmetrized states over the N sites of the A sector and the M sites of the B sector, together with the symmetrized states of the bosonic modes in each sector. Let P_C be the projection operator onto the subspace of the system-environment Hilbert space that is spanned by the cooperative states. Similarly, let $P_N = 1 - P_C$ be the projector onto the ‘normal,’ or non-cooperative subspace. We can then decompose our general Hamiltonian, equation (6), into cooperative sectors (C) and a ‘normal’ sector (N), together with a couplings between these sectors: $H = H_C + H_N + H_{CN}$, where $H_C = P_C H P_C$ is the Hamiltonian confined to the cooperative subspace, $H_N = P_N H P_N$, is the Hamiltonian confined to the normal subspace, and $H_{CN} = P_C H P_N + P_N H P_C$ is the part of the Hamiltonian that couples the cooperative to the normal sector.

In the single-exciton sector, H_C just represents two two-level systems, each coupled to its own environment, but with an enhancement of NM in hopping strength of the exciton from A to B , and with an enhancement of $N(m + 1)(N - m)$ in the interaction strengths for exchange of energy between the A -exciton and the m bosons in the cooperative mode of A ’s environment (similarly for B). In the multiple-exciton sector, H_C is a Hamiltonian that couples two nonlinear harmonic oscillators, where the nonlinearity arises from excitonic interactions; H_C also contains these oscillators’ interactions with their cooperative environments.

The two essential features of the decomposition into cooperative and normal sections are as follows. First, the cooperative Hilbert space has a drastically reduced dimension compared with the full Hilbert space. From the point of view of transport efficiency, this reduced dimension is useful because it prevents the hopping exciton from becoming ‘lost in Hilbert space’: the exciton can inhabit either the A oscillator, or the B oscillator, or it can be transferred to the cooperative environment. The cooperative Hilbert space is too simple, however, to admit such phenomena as localization. In other words, the cooperative Hilbert space is simply too small to get lost in. From the perspective of a scientist investigating the behavior of excitonic hopping, the small size of the cooperative Hilbert space has the advantage that simulating behavior of the cooperative sector is relatively simple compared with a full many-

body treatment.

The second key feature of the full Hamiltonian $H_C + H_N + H_{CN}$ is the relative strength of the dynamics in the different sectors. In the cooperative sector, interactions cooperate coherently, leading to an enhancement of N, M for the interactions of A and B with their respective environments, and an enhancement of NM for the interaction strength. By contrast, the interactions between the cooperative and normal sectors involve mixed symmetries which add incoherently. The terms H_{CN} couple the fully symmetrized sector of Hilbert space to sectors with differing symmetry. These parts of the Hamiltonian induce ‘leakage’ from the symmetric sector. Because the leakage rates do not receive any superradiant enhancement, they can in principle be modelled as a perturbation to the cooperative dynamics. To fully explore the implications of the existence of the cooperative sector, we should construct a master equation using the cooperative sector as ‘system’ and the non-cooperative sector as ‘environment.’ Such a symmetry-based master equation approach will be explored in future work.

Our overall picture, then is as follows: we have a cooperative sector where quantum interference and symmetrization induce enhanced rates of hopping and energy exchange with a symmetrized environment. The cooperative sector has relatively few degrees of freedom. The ‘non-cooperative,’ i.e., ordinary, sector has many more degrees of freedom, but the coupling rates from the cooperative to uncooperative sector can be considerably smaller (e.g, two orders of magnitude smaller if A and B each have a dozen or so sites) than the coupling rates within the cooperative sector. Once a state departs from the cooperative sector, however, it is unlikely to return unless the cooperative sector possesses an intrinsically lower energy than states in the non-cooperative sector, in which case relaxation can drive the system back into the cooperative sector. Resymmetrization by relaxation occurs, for example, in the common case where the lowest energy single exciton state in a ring is the state that is a symmetric superposition of exciton located at each chromophore. (In quantum information, such a state is known as a W state.)

Resymmetrization via relaxation of excitonic states within a ring has the potential to increase the hopping rate by the following mechanism. In situations where the spatial extent of the ring is not small compared with the distance between rings, the couplings of excitons between rings will no longer be symmetric: excitons at the closer edge will couple more strongly than excitons at the further edge. Consequently, the symmetrized state of one ring may have a significant coupling to an asymmetric state of the second ring. As long as these asymmetric states relax to the ground state of the second ring, then such coupling will tend to increase the transfer rate.

A second way that the transfer rate can be enhanced is by coupling of excited states of ring A with excited states of the same symmetry class of ring B . The N -dimensional Hilbert space of single-excitonic states of A decomposes under the symmetric group into the direct sum of the one-dimensional fully-symmetric space – the fully-symmetric state described

above – plus the $N - 1$ dimensional antisymmetric subspace. If the ambient temperature is higher than the energy splitting between the symmetric ground state of the single exciton sector, and the higher energy states within that sector, a further enhancement mechanism is the symmetric coupling of higher energy single exciton states in ring A with excited states *with the same symmetry type* in sector B. The transfer rate due to such couplings between states of the same symmetry exhibits the *same* MN -fold enhancement as the couplings between the symmetrized ground states. Whether or not such interplay between excited single-exciton states plays a significant role depends on the strength of the various couplings compared with each other and compared with the ambient temperature. The full effects of differing symmetry types in such complex quantum systems lies outside of the scope of the current paper and will be dealt with in a further work.

APPLICATION TO NANO-ENGINEERED LH2 COMPLEXES

Even without a detailed master equation treatment, we can still apply the concept of a ‘speeded up’ cooperative sector to experimentally observed effects [10] reported an anomalously long diffusion length in engineered arrays of LH2 complexes. Two systems were investigated, a two-dimensional crystal of LH2 complexes, and an effectively one-dimensional nanofabricated array of such complexes. In both systems diffusion lengths of up to a micron were reported.

On the face of it, this diffusion length seems absurdly long: LH2 complexes are about 7 nanometers in diameter and 6.8 nanometers in height. A diffusion length of a micron requires $O(10^5)$ exciton hopping steps over the course of 1 to 1.5 nanosecond lifetime with an effective displacement of about 300 units away from its original location. If the dynamics is described by diffusive hopping from complex to complex, such a diffusion length would require hopping times of 10 to 15 femtoseconds. By contrast, detailed calculations and experimental observation of naturally occurring arrangements of LH2 complexes suggest a hopping time of around 5 picoseconds, a difference of almost three orders of magnitude.

Cooperative quantum behavior suggests an alternative explanation for these anomalous diffusion lengths. Each LH2 complex contains a ring of $N = 18$ bacterial chlorophylls with a resonant frequency for light with a wavelength of 800 nm, and 9 chlorophylls with a resonant frequency at 850 nm. Thus, we may reasonably expect a significant enhancement from cooperative coherent effects. The frequencies and linewidths of the LH2 complexes in the crystals and nanofabricated arrays are essentially the same as in native LH2. The exact effect of cooperative behavior depends on the precise arrangement of LH2 complexes in each array, and is difficult to calculate. From the above analysis, however, it is reasonable to suppose that cooperative behavior enhances the actual LH2 to LH2 hopping rate by a factor α . For example, taking the ‘native’ value of 5 picoseconds for the unhanced hopping

time, $\alpha = 5$ represents an enhanced hopping time of around 1 picosecond.

Even if $\alpha = 10$, we are still a factor a hundred away from the 10-15 femtosecond hopping rate required for an incoherent hopping process to explain the anomalous diffusion rate. Now, however, the speeded up cooperative hopping allows a second effect of quantum coherence to come into play. Let the lifetime of the exciton be T and the decoherence time for the hopping process be τ . We do not know the decoherence time for hopping in such engineered arrays, but in other photosynthetic systems it ranges from picoseconds to tens of picoseconds. Call the hopping rate in the absence of cooperative effects γ , and the hopping rate in the presence of cooperative effects is $\alpha\gamma$. If $\alpha\gamma$ is significantly greater than $1/\tau$, then the exciton hops *coherently* through the array for about $\ell = \alpha\gamma\tau$ steps. In other words, for brief periods of time, the exciton is performing a quantum walk. During this time, as is usual with quantum walks, the coherent diffusion time goes linearly in the number of steps, rather than as the square root of the number of steps. For times longer than the decoherence time, the hopping becomes incoherent. We can therefore model the combination of coherent and incoherent hopping as diffusive transport with a hopping rate equal to the original, unhanced rate γ , but with an increased step size of ℓ . We see that the effect of coherent hopping to increase the effective diffusion length.

Let the net number of units that the exciton has to diffuse before decaying be L . In the case of the LH2 complexes, L is on the order of 300. The effect of cooperative coherent behavior is to reduce the total number of required incoherent hopping events from L^2 to $L^2/\ell^2 = L^2/(\alpha\gamma\tau)^2$. The total number of incoherent hopping events in the coherence-enhanced diffusion is no greater than the overall lifetime times the hopping rate, $T\gamma$. Putting these relations together, to explain the anomalously long diffusion rate in terms of cooperative coherent behavior, we require that the dimensionless step size ℓ be at least

$$\ell = \alpha\gamma\tau > \frac{L}{\gamma^{1/2}T^{1/2}}. \quad (7)$$

For $L = 300$, $T = 1$ nanosecond, $\gamma^{-1} = 5$ picoseconds, this requires that $\alpha\tau$ be greater than 100 picoseconds. For example, if the coherent enhancement factor $\alpha = 5$, a reasonable number given that there are 18 LH2 chlorophyll participating in transport at 800 nm, and 9 participating at 850 nm, then the hopping decoherence time must be at least 20 picoseconds. If, by contrast, in the packed arrays of crystalline and nanofabricated LH2, $\gamma = 2$ picoseconds, then $\alpha\tau$ need only be around 20 picoseconds. Pending more exact observations of the hopping decoherence rate in LH2 arrays, and more exact calculations of the actual coherent enhancement, such numbers seem entirely reasonable: only moderate coherent enhancements are required to explain the three orders of magnitude increase of the apparent hopping rate in nano-engineered LH2 arrays.

CONCLUSION

This paper presented a simplified discussion of the effects of symmetry on hopping processes and environmental interactions. Just as symmetry provides an enhancement of super-radiance, it can, under the proper circumstances, lead to supertransport; i.e., an effective enhancement of hopping rates and of coherent and incoherent interactions with environmental modes. Conversely, antisymmetry can significantly reduce effective environmental interactions and enhance excitonic lifetimes. The interplay between symmetry and antisymmetry properties of delocalized excitonic states in photosynthetic complexes can be thought of as nature's use of quantum coherence effects.

Full dynamical analysis of the effects of the symmetry breaking part of the Hamiltonian will be the subject of a subsequent work [19]. Silbey and co-workers constructed a theory for multichromophoric Forster energy transfer that can provide a useful model for studying enhanced cooperative transport in disordered materials and photosynthetic complexes assuming that coupling between collective donor and acceptor chromophores can be treated perturbatively [22]. Generally, in addition to important effects of disorders and phonon-bath couplings, the geometrical structure of donor and acceptor in molecular aggregates could play a significant role when one considers excitonic transfer beyond dipole approximation [18]. Recently there have been a great deal of interest to study excitonic transport in non-perturbative and non-Markovian regime [8, 9]. Similar approaches for exploiting certain symmetry of chromophoric structures and their coherence/decoherence dynamical interplay [3, 24] could lead to design principles for engineering artificial excitonic systems, such as quantum dot structures and organic materials, for efficient excitation energy absorption, emission, storage, and transport. The observation of anomalously long diffusion lengths in LH2 arrays suggests that even moderate degrees of coherent cooperation can significantly enhance the performance of engineered excitonic systems.

Acknowledgements: The authors acknowledge the support of the W.M. Keck foundation, NSERC, Jeffrey Epstein, ENI, and Lockheed Martin.

[1] G.S. Engel, T.R. Calhoun, E.L. Read, T.-K. Ahn, T. Mancal, Y.-C. Cheng, R.E. Blankenship, and G.R. Fleming, *Nature* **446**,

782 (2007).
 [2] H. Lee, Y.-C. Cheng, and G.R. Fleming, *Science* **316**, 1462 (2007).
 [3] M. Mohseni, P. Rebentrost, M. Mohseni, S. Lloyd, and A. Aspuru-Guzik, *J. Chem. Phys.* **129**, 174106 (2008); P. Rebentrost, M. Mohseni, S. Lloyd, I. Kassal, and A. Aspuru-Guzik, *New J. of Phys.*, **11**, 033003 (2009); P. Rebentrost, M. Mohseni, and A. Aspuru-Guzik, *J. of Phys. Chem. B* **113**, 9942 (2009).
 [4] M.B. Plenio and S.F. Huelga, *New J. Phys.* **10**, 113019 (2008); F. Caruso, A. W. Chin, A. Datta, S. F. Huelga, M. B. Plenio, *J. of Chem. Phys.* **131**, 105106 (2009).
 [5] I. Mercer, Y. El-Taha, N. Kajumba, J. Marangos, J. Tisch, M. Gabrielsen, R. Cogdell, E. Springate, and E. Turcu, *Phys. Rev. Lett.* **102**, 057402 (2009).
 [6] E. Collini and G. D. Scholes, *Science* **323**, 369 (2009).
 [7] E. Collini, C. Y. Wong, Krystyna E. Wilk, P. M. G. Curmi, P. Brumer and G. D. Scholes, *Nature*, **463**, 7281 (2010).
 [8] S. Jang, Y. Cheng, D. R. Reichman, and J. D. Eaves, *J. Chem. Phys.* (Communication) **129**, 101104 (2008).
 [9] A. Ishizaki, G.R. Fleming, *J. Chem. Phys.* **130**, 234110 and 234111 (2009); A. Ishizaki, G.R. Fleming, *Proc. Natl. Acad. Sci.*, **106** 17255 (2009).
 [10] M. Escalante, *et al.*, *Nano Lett.* **10**, 1450 (2010).
 [11] R.H. Dicke, *Phys. Rev.* **93**, 99-110 (1954).
 [12] N.E. Rehler, and J.H. Eberly, *Phys. Rev. A* **3**, 1735-1751 (1971).
 [13] H. Fidler, J. Knoester, D.A. Wiersma, *J. Chem. Phys.* **95** 7880 (1991).
 [14] Y. Zhao, T. Meier, W.M. Zhang, V. Chernyak, S. Mukamel, *J. Phys. Chem. B* **103** 3954 (1999).
 [15] M. Palacios, F. L. de Weerd, J. A. Ihalainen, R. van Grondelle, and H. van Amerongen *J. Phys. Chem. B* **106**, 5782-5787 (2002).
 [16] G. Jin, P. Zhang, Y. Liu, and C. P. Sun, *Phys. Rev. B* **68**, 134301 (2003).
 [17] W. Strek, *Phys. Lett. A* **62**, 315-316 (1977).
 [18] G. D. Scholes, *Chem. Phys.* **275**, 373-386 (2002).
 [19] M. Mohseni and S. Lloyd, in preparation.
 [20] G. D. Scholes and G. R. Fleming, *J. Phys. Chem. B* **104**, 1854 (2000).
 [21] G. D. Scholes, X. J. Jordanides, and G. R. Fleming, *J. Phys. Chem. B* **105**, 1640 (2001).
 [22] S. Jang, M.D. Newton, R.J. Silbey, *Phys. Rev. Lett.* **92**, 218301 (2004).
 [23] T. Hu, A. Damjanovic, T. Ritz, and K. Schulten, *Proc. Natl. Acad. Sci.* **95**, 5935 (1998).
 [24] J. Cao, and R. Silbey, *J. Phys Chem. A* **113**, 13825 (2009).